

Uitgegeven den

1 6 JAN 1947

PATENT SPECIFICATION

583,477

Application Date: Oct. 4, 1943.

No. 16225/43.

Complete Specification Left: Oct. 2, 1944.

Complete Specification Accepted: Dec. 19, 1944.

Bibliotheek
Bur. Ind. Eigendom

PROVISIONAL SPECIFICATION

1 3 JAN 19 '48



Improvements in or relating to the Manufacture of Phosgene

We, DENNIS BRINDRIT, a British Subject, of 39, Alexandra Road, Thornton, near Blackpool, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the nature of this invention to be as follows:—

This invention relates to an improved process for the manufacture of phosgene.

It is well known that phosgene is manufactured from the reaction of chlorine with carbon monoxide in the presence of a catalyst. In such processes it is usual to mix dry chlorine with a slight excess of dry carbon monoxide, e.g. in the form of producer gas, and to pass the mixture at approximately atmospheric pressure and at a temperature of 150° to 200°C. through one or more reaction vessels containing a catalyst, which may be charcoal. The combination of the chlorine and carbon monoxide takes place readily, but for commercial operation it has been found necessary to provide bulky reaction vessels which necessitates a considerable amount of attention being paid to control of the process. Further, the treatment of the phosgene coming from the reaction vessels in order to liquefy it for transport, or to render it available for use in other manufacturing processes, frequently involves a compression step which has many undesirable features.

We have now found, unexpectedly, that many marked advantages accrue when the reaction between chlorine and carbon monoxide in the presence of a catalyst is carried out under a substantially superatmospheric pressure.

For example, by effecting the reaction under a pressure of 20 lbs. per square inch (gauge pressure) we have found that the reaction vessel need only be one-fortieth of the size of that required for the same output when working at atmospheric pressure. With still higher pressures, say up to 150 lbs. per square inch, even smaller vessels may be used. With such reduced sizes of reaction vessel considerably less supervision and attention is needed, and the requisite control of the temperature of the vessels is very much

more easily effected than in the case of the larger vessels which have been used hitherto. Further, the recovery, in a transportable form of a large proportion of the phosgene produced is attained by a simple cooling of the gases from the reaction vessel.

In carrying out a process according to the invention, various forms of apparatus may be used. For example, we have found it convenient to use as reaction vessels, sets of lead-lined mild steel tubes packed with a catalyst such as activated charcoal, and provided with means for supplying cooling water to the outside of the tubes in order to effect the necessary temperature control. Alternatively, an annulus packed with catalyst and cooled on both external and internal surfaces may be used. Advantageously the process is carried out in two such reaction vessels arranged in series, the first being operated at a higher temperature than the second. With this arrangement and using a slight excess of CO we have found it possible to obtain a final product substantially free from unreacted chlorine. Suitable operating conditions whereby this result can be achieved are conditions such that the exit gas from the first tower has a temperature not exceeding 280°C., the gas being then cooled to approx. 30°C. before delivery to the second tower. The exit gas from the second tower should have a temperature not exceeding 60°C.

The dry reacting gases may be supplied to the reaction vessels in any convenient way. For example, the chlorine may be vaporised from a cylinder or it may be taken from a manufacturing process, dried, and then compressed to the required pressure for supply to the reaction vessel. The carbon monoxide may be used as producer gas, or it may be prepared as a high strength gas from oxygen and coke. In either case it is freed from dust, etc., dried and compressed. The separately compressed gases are then mixed and passed to the reaction vessel. Alternatively, the dry gases may, if desired, be mixed at normal pressure and the mixture then compressed for supply

[Price 1/-]

BEST AVAILABLE COPY

to the reaction vessels.

The gas issuing from the reaction system may, with advantage, be used directly in any appropriate reaction for the manufacture of another chemical. For this purpose it may be used under the pressure maintained in its manufacture or after any appropriate reduction.

Alternatively, if it is desired to transport or store the phosgene the major portion

may be readily obtained as liquid by a simple cooling, and the liquid transferred directly to suitable containers. Any residual phosgene remaining in the tail gas can be recovered in an appropriate absorption system.

Dated the 4th day of October, 1943.

J. W. RIDSDALE,

Solicitor for the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Phosgene

We, DENNIS BRUNDRIE, a British Subject, of 39, Alexandra Road, Thornton, near Blackpool, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1. do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to an improved process for the manufacture of phosgene. It is well known that phosgene is manufactured by the reaction of chlorine with carbon monoxide in the presence of a catalyst. In such processes it is usual to mix dry chlorine with a slight excess of dry carbon monoxide, for example in the form of producer gas, and to pass the mixture at approximately atmospheric pressure and at a temperature of 150°C. to 200°C. through one or more reaction vessels containing a catalyst, which may be charcoal. The combination of the chlorine and carbon monoxide takes place readily, but for commercial operation it has been found necessary to provide bulky reaction vessels which necessitate a considerable amount of attention being paid to control of the process. Further, the treatment of the phosgene coming from the reaction vessels in order to liquefy it for transport, or to render it available for use in other manufacturing processes, frequently involves a compression step which has many undesirable features. It is also necessary to treat the tail gas from the liquefaction step either to recover the phosgene by adsorption, for example on active charcoal, or to strip it from the effluent gas by contact with aqueous caustic soda. The compressors used in the liquefaction stage cause the reaction system to be maintained under slight suction so that leakage of air into the system may occur, causing an increase in the volume of tail gas, thus increasing the load on the recovery or stripping system. It is evident that any

method of diminishing the volume of the tail gas will improve this part of the process.

According to the present invention a process for the production of phosgene comprises reacting chlorine with carbon monoxide in the presence of a catalyst for the reaction under a substantially superatmospheric pressure.

It has been found unexpectedly that many marked advantages accrue by using a substantially superatmospheric pressure in this reaction. It is, of course, well known that in a balanced gas reaction of the type $A + B = C$ an increase in pressure will favour the proportion of A and B converted to C. In the particular case of the production of phosgene from chlorine and carbon monoxide, however, no advantage was to be expected on these grounds since even at atmospheric pressure and at the temperatures normally employed in the process substantially complete conversion to phosgene is achieved. In fact, no significant increase in conversion efficiency does result by using the superatmospheric pressures with which the present invention is concerned. On the other hand advantages do accrue in that the interior of the reaction system is maintained at a pressure above atmospheric, so that it is possible to avoid leakages of air into the system with the consequent increase in volume of the tail gas and thus decreased load on the adsorption or stripping system. Further, the greater thermal conductivity of the reaction gases at the increased pressure allows the construction of the catalyst chamber to be modified to give increased cooling efficiency, and this in turn enables a more active catalyst to be used than has hitherto been possible without causing undesirable increases in catalyst temperature. Thus an activated coconut charcoal catalyst can be used where hitherto less efficient unactivated wood charcoal has been necessary to avoid too great an evolution of heat.

As a result of all these factors it has

been found that a very considerably enhanced output using a given volume of catalyst can be achieved, or alternatively, the same output can be obtained with a very much diminished catalyst volume. Thus, for example, by effecting the reaction under a pressure of 20 lbs. per square inch (gauge pressure) it has been found that the reaction vessel need only be one-eighth of the size of that required for the same output when working at atmospheric pressure. With still higher pressures, say up to 150 lbs. per square inch (gauge pressure) even smaller vessels may be used.

Still further advantages accrue in that with such reduced size of reaction vessel considerably less supervision and attention are needed, and the requisite control of the temperature of the vessel is rendered easier on this account also. Further, the liquefaction of a large proportion of the phosgene produced can be attained by a simple cooling of the gases from the reaction vessel.

In carrying out a process according to the invention, various forms of apparatus may be used. For example, it has been found convenient to use as reaction vessels sets of lead-lined mild steel tubes packed with a catalyst such as activated charcoal, and provided with means for supplying cooling water to the outside of the tubes in order to effect the necessary temperature control, that is, to maintain the temperature of the tubes below about 280°C. Unlined steel tubes may also be used, although a lower maximum temperature, about 150°C., is set by corrosion difficulties. Alternatively, an annulus packed with catalyst and cooled on both external and internal surfaces may be used. Advantageously the process is carried out in two such reaction vessels arranged in series, the second being operated at a lower temperature than the first. With this arrangement and using a slight excess of CO it is possible to obtain a final product substantially free from unreacted chlorine. Suitable operating conditions whereby this result can be achieved are conditions such that the exit gas from the first tower has a temperature not exceeding 280°C. in the case of a lead lined chamber, or 150°C. in the case of an unlined mild steel chamber, the gas being then cooled to a temperature not exceeding 60°C., suitably to approximately 30°C., before delivery to the second tower.

Liquid phosgene can then be recovered from the exit gas by cooling, for example to -40°C. to -55°C. and separating out the phosgene which liquefies. The tail gas can then either be

passed over a charcoal adsorption unit to adsorb the small amounts of phosgene in it for subsequent recovery, or the tail gas from the liquefaction may be washed with aqueous caustic alkali to destroy the phosgene therein.

The process may be carried out with a pressure in the reaction vessels as low as 20 to 25 lbs. per square inch (gauge pressure), although if desired, much greater pressures up to 300 lbs. per square inch (gauge pressure) may be used. In general, however, gauge pressures of the order of 150 lbs. per square inch will be found most suitable since all the advantages of the invention are realised without incurring a greater expense in compressing the reaction gases than is warranted by the improved recovery of the phosgene from the tail gases.

The dry reacting gases may be supplied to the reaction vessels in any convenient way. For example, the chlorine may be vaporised from a cylinder or it may be taken from a manufacturing process, dried, and then compressed to the required pressure for supply to the reaction vessel. The carbon monoxide may be used as producer gas, or it may be prepared as a high strength gas from oxygen and coke. In either case it is freed from dust and the like, dried and compressed. Compressing the reactants does not offer the great difficulties and inconveniences associated with the compression of phosgene. The separately compressed gases are then mixed and passed to the reaction vessel. Alternatively, the dry gases may, if desired, be mixed at normal pressure and the mixture then compressed for supply to the reaction vessels.

The gas issuing from the reaction system may, with advantage, be used directly in any appropriate reaction for the manufacture of another chemical. For this purpose it may be used under the pressure maintained in its manufacture or after any appropriate reduction.

Alternatively, if it is desired to transport or store the phosgene the major portion may be readily obtained as liquid by a simple cooling below the dew point, for example -40°C. to -55°C., and the liquid transferred directly to suitable containers. Any residual phosgene remaining in the tail gas can be recovered in an appropriate adsorption system.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of phosgene which comprises reacting

chlorine with carbon monoxide in the presence of a catalyst for the reaction at a substantially superatmospheric pressure.

2. A process according to claim 1 carried out at a pressure between 20 lbs. per square inch (gauge pressure) and 300 lbs. per square inch (gauge pressure).

3. A process according to claim 1 or claim 2 carried out at a pressure of approximately 150 lbs. per square inch (gauge pressure).

4. A process according to any of the preceding claims in which producer gas is the source of carbon monoxide.

5. A process according to any of the preceding claims in which activated charcoal is used as the catalyst.

6. A process according to any of the preceding claims in which reaction is effected at a temperature below 280°C.

7. A process according to any of the preceding claims 1 to 5 in which the reaction is carried out in two reaction

vessels in series, the first of which is maintained at a temperature not exceeding 280°C. and the second at a temperature not exceeding 60°C.

8. A process according to any of the preceding claims, followed by the step of recovering liquid phosgene from the gaseous reaction products by cooling them without subjecting them to further compression.

9. A process according to claim 8 in which the gases are cooled to between 35 - 40°C. and -55°C.

10. A process for the production of phosgene substantially as hereinbefore described.

11. Phosgene whenever obtained by a process according to any of the preceding claims.

Dated the 2nd day of October, 1944.

J. W. RIDSDALE.

Solicitor for the Applicants.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.